UNPUBLISHED PRELIMINARY DATA

UNIVERSITY OF WISCONSIN

THEORETICAL CHEMISTRY INSTITUTE

58 p

TYPE OF REPORT:	SEMI-ANNUAL REPORT to National Aeronautics and Space Administration
NUMBER OF REPORT:	Five (5)
PERIOD REPORT COVERS:	1 July 1964 through 31 December 1964
GRANT NUMBER:	NsG-275-62
DATE:	31 December 196[redacted]

SIGNATURES:

[redacted]

Joseph O. Hirschfelder

Joseph O. Hirschfelder
Principal Investigator

CR 60159

C. F. Curtiss

C. F. Curtiss
Principal Investigator

FACILITY FORM 602

N66-85664
(ACCESSION NUMBER)

58
(PAGES)

CR 60159
(NASA CR OR TMX OR AD NUMBER)

(THRU)

None
(CODE)

(CATEGORY)

[redacted]

to predict the many types of applications which might result: the development of new types of materials[1]; the development of new types of propulsion systems[2]; the development of new types of fuels, etc. The advantage of such a theoretical development based upon the fundamental laws of physics is that it is equally applicable to any conditions of temperature, pressure, or radiation. We are also hoping that our work will have biological applications[3].

Whereas theoretical physics has received a great deal of attention and a large amount of financial assistance, theoretical chemistry has been largely neglected. Theoretical chemistry starts with the laws of nature, which are now known. Indeed, we can write down the equations whose solutions would give us the chemical and physical properties which we desire. The solution to these equations will require improved mathematical techniques and the large scale useage of high-speed computing machines.

We do not anticipate much additional expansion of our group. However, we still have need for a quantum chemist who is expert on the numerical solutions of Schrödinger Equations. Progressively, as we perfect our mathematical methods, we will have heavier use of

- - - - -

1. As you know, one of my former students, R. H. Wentorf, has already discovered a material harder than diamonds, borazone.

2. During World War II, J. O. Hirschfelder and C. F. Curtiss developed a system of interior ballistics of guns which has been adopted by all the military services. Subsequently they developed the theory of flame propagation, which was required for the development of ram-jets for the Navy BUMBLEBEE program.

3. We are setting up a small quantum-biochemical program under the direction of Dr. John Graves and under the auspices of N.I.H.

NASA SEMI-ANNUAL PROGRESS REPORT

INTRODUCTION

We are making excellent progress. We have an excellent group. Everyone knows what he needs to do and is doing it. The research is very difficult, but substantial progress is being made. You have told us to build solid for the long pull, rather than waste our efforts by being flashy. We are taking you at your word.

The attached letters from the Dean of the Graduate School, the Chairman of the Department of Chemistry, and the Chairman of the Department of Chemical Engineering indicate the close ties which we have with many of the University Departments and the cooperation which we are receiving from the University of Wisconsin administration. In addition, we are working very closely with the Army Mathematics Research Center at the University of Wisconsin. Next fall the Army Mathematics Research Center is arranging a symposium on perturbation theory based upon the mathematical problems and interests of our Institute. The Army Mathematics Research Center is joining with us in bringing from the University of California the great Japanese mathematical physicist, Tosio Kato, for the period July through December, 1965, provided that his health permits.

We want to take this opportunity to thank NASA for a wonderful opportunity to carry out a very important long-range basic research program, which, if successfully completed, will give us an insight into the chemical and physical properties of materials in any environment of temperature, pressure, or radiation. It is hard high speed computing equipment. Our computing needs should reach a peak by 1967, when our remote control computer is scheduled for installation.

Final plans are being completed for the new chemistry building. The Theoretical Chemistry Institute will occupy the eighth and one-third of the ninth floors. The Department of Chemistry is taking over our space in the present unit and giving us in return an equal amount of space in the new unit. The rest of our space in the new unit is financed by a grant of $442,760 from NASA. At the present time our group is very crowded, with all of our graduate students and our report processing located in an old frame house across the street.

RESEARCH INTERESTS OF THE THEORETICAL CHEMISTRY INSTITUTE STAFF

There is a wide range of research at the Theoretical Chemistry Institute. W. Byers Brown, Saul T. Epstein, J. O. Hirschfelder, and Daniel D. Konowalow are currently working on molecular and intermolecular quantum mechanics problems. Frank C. Andrews and C. F. Curtiss are concerned with statistical mechanics and transport properties of gases and plasma. Richard B. Bernstein, C. F. Curtiss, and Stuart E. Lovell are interested in molecular beams and scattering theory. John E. Harriman is working on electron-spin resonance and quantum mechanical density matrices. John Graves is trying to apply quantum and statistical mechanics to biological problems. The following is a summary of the detailed research interests of each of the staff members:

FRANK C. ANDREWS

Current research ~~activities are on~~ in the non-equilibrium statistical mechanics of dense classical gases. The formulation of a functional equation for reduced, several-particle distribution functions and the formulation of a generalized Boltzmann equation for the one-particle distribution function have been obtained from the reduced Liouville (or BBGKY) equation in the form of a density expansion.[1] The stress in this work is on understanding the physical implications of the results and on mathematical simplicity. It is felt, for example, that the range of validity of Bogoliubov's hypothesis[2] that f_s rapidly becomes a functional of f_1 is now understood in terms of the initial information available about the system.

An investigation is now under way to see if the statistical mechanical expressions for the transport properties in gases cannot be obtained as direct consequences of the mechanics of the molecules without the usual extensive labor.[3] It is hoped that this, coupled

- - - - -

1. F. C. Andrews, "On the Solution of the BBGKY Equations for a Dense Classical Gas", WIS-TCI-70, 30 October 1964.

2. N. N. Bogoliubov, "Problems of a Dynamical Theory in Statistical Physics", 1946, English translation in Studies in Statistical Mechanics, vol. 1, North-Holland Publishing Co., Amsterdam, 1962.

3. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, New York, 1954), Chap. 7.

with work on the establishment of the usual hydrodynamic equations for gases, will lead to insights into the onset of turbulence and similar phenomena. Many extensions of the ordinary Chapman-Enskog theory would either be made simpler or possible if a simple, physical formulation of Chapman-Enskog results were obtainable. It is felt that the entire field of the molecular theory of gas dynamics is ripe for unification and extension.

Another area in which work might progress in the future is that of the statistical mechanical theory of dielectric relaxation in liquids. Such a basic question as "What are the necessary and sufficient conditions for the validity of the Debye equations?" have yet to be answered. This work would be done in conjunction with Prof. Worth E. Vaughan of the Chemistry Department.

There is interest in a number of problems in the statistical mechanical theory of the mechanical properties of polymer solutions.

There is also a continuing interest in certain more or less pedagogical problems in both classical and non-equilibrium thermodynamics.

RICHARD B. BERNSTEIN

The writer's research program in the field of elastic and inelastic molecular scattering receives about one-third of its financial support from the NASA grant. These funds are used primarily in connection with the theoretical and computational aspects of the research (which is, however, predominantly experimental in nature).

The main effort is directed toward a quantitative understanding of the problem of rotational excitation and beam scattering of diatomic molecules by atoms. Two approaches are being investigated in parallel. First, the rigorous (but computationally overwhelming) S-matrix or time-independent method; and second, the approximate (but computationally feasible) time-dependent perturbation method known as the "sudden approximation".

The two studies are complementary. At low collision energies the time-independent procedure is most feasible of practical solution while the sudden approximation is inapplicable, as its assumptions have lost their validity. At higher energies, however, where the S-matrix method in its usual detailed sense becomes computationally futile, the validity of the sudden approximation should be best (and it is even simpler in its numerical execution). It is important to ascertain the sensitivity of the computed results (for each of these methods) to the anisotropy and magnitude of the intermolecular potential. It is hoped that it will eventually be possible to come to a practical decision as to the range of utility of these procedures and the degree of confidence which may be attached to transition probabilities and cross sections obtained from each of them, in appropriate energy ranges.

The work on the sudden approximation has been carried out in collaboration with Dr. K. H. Kramer. Additional work, not yet in final form, has been carried out by Dr. J. L. J. Rosenfeld. The program is to be extended with the collaboration of Dr. William A. Lester and Mr. John H. Huntington.

The remainder of the research effort receiving NASA support is concerned with the elastic scattering of atoms, molecules and ions in relation to the interaction potential. The feature which is being given special consideration is the extrema behavior in the total cross sections, i.e. the maxima and minima in the elastic impact spectrum at low collision energies. These maxima may be correlated with the bound states of the composite system. From the extrema-velocities it is possible to deduce the magnitude of the product of the potential well depth times the collision diameter, for a potential of any given functional form.

In anticipation of new experiments on low energy ion-atom scattering now being initiated in a number of laboratories, computations have been carried out by Dr. G. G. Weber and the writer on scattering cross sections for $Li^{+} - He$. A number of reasonable alternative forms for the potential energy of this system were chosen. The general features of the computed results were in accord with previous findings for neutral systems. It was concluded that the extrema should be observable at energies below 10 ev and their locations would serve as sensitive indicators of the shape of the potential in the region of its minimum. A new calculation is underway to deal similarly with proton-helium scattering. For the H^+ - He system a fairly reliable SCF - calculated potential function has recently been evaluated by S. Pyerimhoff of the University of Chicago, so that the predicted scattering cross sections should be of quite reasonable accuracy and should serve as a good guide to future experiments. Accurate experimental data on both differential and total cross sections, when available, in the low energy regime could, in turn, be used to confirm or improve upon the potential. The proton-helium system may well turn out to be a very important one, having here an *ab initio* calculation of a potential function to be compared with one obtainable from scattering data.

In addition to the specific calculations outlined above certain general aspects of the theory of the extrema-effect in atom-atom scattering cross sections and their relation to the vibrational force constant of the diatom are being investigated, with the help of Mr. T. J. O'Brien. The influence of the curvature of the potential function at its minimum upon the spacing of the extrema in an impact spectrum is of considerable interest. It is hoped that this work will lead to practical methods which will allow the extraction of the maximum amount of information about the interaction potential from total elastic cross sections in the thermal energy range.

In addition to the work which has been described above a considerable amount of supporting computational work is being carried out in connection with the experimental program on elastic, inelastic and reactive scattering of molecular beams. Included in the bibliography are a number of entries describing work which is primarily experimental in nature but which has received partial support from NASA (see Appendix C).

W. BYERS BROWN

The bulk of my present research in molecular quantum mechanics is concerned with the application of perturbation theory to stationary state problems.

1) Perturbation theory of extended Hartree-Fock method. (In collaboration with Mr. George V. Nazaroff and Dr. Delano P. Chong).

In the ordinary restricted Hartree-Fock approximation electrons are paired in the same spatial orbitals with opposite spin. Some degree of correlation is introduced by allowing the orbitals to be different and of arbitrary symmetry, and then picking out a wave function having the correct total symmetry by means of a projection operator (extended Hartree-Fock). Non-linear coupled integro-differential equations for the extended Hartree-Fock orbitals can be derived by the variation principle. I am currently investigating the 1/Z perturbation analysis of the equations, and in particular those of the first order, in collaboration with Mr. George V. Nazaroff (He and two-electron atoms) and Dr. Delano P. Chong (Li,Be). The results so far are theoretically of great interest and numerically very encouraging.

2) Perturbation theory of carbon monoxide based on nitrogen (In collaboration with Mr. Tai Yup Chang)

The direction of the small dipole moment of CO (0.12D) has been the subject of controversy for some years. An indirect experimental result due to Townes, et. al. (1958) led to the polarity C^-O^+ in contradiction to chemical intuition. Early Hartree-Fock calculations by Ransil (1960) supported the experimental assignment, but more accurate calculations with a larger basis set (Nesbet et. al. 1960, 1963; Huo 1964) lead to a dipole with about the same magnitude but opposite sign from the experimental.

The object of the present work is to develop a perturbation theory of CO based on N_2. Since the molecules are isoelectronic, the perturbation is the sum of one-electron operators. The energy and dipole can be expanded in powers of a perturbation parameter $\lambda = (Z_A - Z_B)/(Z_A + Z_B)$ which is 1/7 for the CO/N_2 case. Only alternate powers of λ appear for symmetry reasons, so that if only the leading terms of the perturbation expansion are considered, the error is only of order λ^2 or about 2 per cent in a favourable case. The hope is to show clearly the origin and sign of the dipole moment, and also to compare the dissociation energies and equilibrium distances in the two molecules.

If the calculations are successful I have plans to extend them to treat borazine, $B_3N_3H_6$, with benzene, C_6H_6, as the unperturbed system, and borazon $(BN)_\infty$ with diamond as the unperturbed system.

3) Perturbation expansion of molecules based on the united atom

(In collaboration with Mr. Sungwoon Kim)

The general expansion of the electronic energy W of a molecule about the united atom in powers of the internuclear distances was first developed by W. Bingel (1959). However, the coefficient W_3 of the term in R^3 for a diatomic molecule was subsequently shown to be incorrect by the author and E. Steiner (1961, 1963). The correct expression for W_3 for a diatomic molecule has been obtained heuristically, and current research is directed towards the following objectives:

(a) A direct proof of the diatomic formula for W_3.

(b) Generalization of the formula to polyatomic molecules.

(c) An understanding of the dependence of the coefficients W_n on the atomic numbers Z_a, Z_b, etc.

(d) The expansion of other properties such as dipole moment and polarizability.

(e) Investigation of the non-analytic nature of $W(R)$.

4) <u>Perturbation theory of force constants</u> (In collaboration with Dr. Margaret Benston)

The calculation of expectation values of one-electron operators for atoms has been greatly stimulated by the work of Dalgarno and collaborators, who have applied perturbation theory and introduced an Interchange Theorem. The object of the present work is to apply these techniques to the calculation of force constants of molecules. Force constants can be written as the sum of a first and a second order property, both of which involve only one-electron operators.

5) <u>Perturbation treatment of electron repulsion in the hydrogen molecule</u> (In collaboration with Messrs. Robert L. Matcha, William D. Lyon and Bowen Liu).

The unexpected success of the $1/Z$ perturbation expansion in the treatment of two-electron atoms (Hylleraas 1930; Scherr and Knight 1963) suggests that an analogous treatment be attempted for molecules. The major difficulty lies in the fact that one exact solution of the unperturbed problem, H_2^+, although known, is unwieldy and must be handled numerically. Our effort has therefore bifurcated into two:

(a) Single perturbation with exact H_2^+ basis. (Robert L. Matcha)

(b) Double perturbation treatment with simple molecular orbital basis function. The second perturbation is due to the inexact treatment of the two-centre coulomb potential by the m.o. function. (William D. Lyon and Bowen Liu)

6) <u>Investigation of Hartree-Fock equations</u> (In collaboration with Miss Pearl S. C. Wang)

The author has recently obtained one exact solution of the Hartree-Fock equation for the Frost delta-model of a two-electron atom. In collaboration with Miss Wang the exact solution of the corresponding model for two-electron diatomic molecules has been obtained. Certain features of the model remain to be investigated, but current interest has been diverted to another aspect of Hartree-Fock equations discovered by Kelly (1963). Namely, that all the virtual solutions of the equation appear to lie in the continuum. This point is being investigated analytically and numerically in collaboration with a mathematician, Dr. J. B. McLeod at present at the University of Wisconsin Mathematics Research Center.

7) <u>First-order perturbation equation for helium</u> (In collaboration with Mr. Ronald J. White)

The analytical solution of the Schrödinger equation for a two-electron atom (He-like) has never been found despite strenuous efforts by many eminent theoreticians starting with Heisenberg and Hylleraas in the 1920's. This may be too ambitious an aim with present day mathematics. However, even the much simpler inhomogeneous first-order perturbation equation has not been solved to date. It is known that the solution of this equation allows one to calculate the energy of any many-electron atom to third order. The only other practical approach is by means of the variation principle, which gives excellent eigenvalues but poor eigenfunctions.

Hope that the first-order equation may be soluble has recently been stimulated by the exact solution of the first-order equations for two similar models by the author and Ronald J. White. The models are the Frost delta-model and the Hooke's law atom, previously discussed numerically by Sinanoğlu and Kestner (1962). Further details of the second model, in particular the natural spin-orbitals, are still being investigated. The idea is to apply the knowledge gained from these models to the actual two-electron Coulomb law atom.

<u>Long Range Research Program</u>

This depends on the outcome of investigation number 7 above. If the solution of the first-order He equation were obtained, the application of the results to the many-electron atoms is then straight forward, and would be pursued. No doubt the form of the first-order wave function for atoms would suggest new basis functions for the treatment of molecules.

C. F. CURTISS

We have continued our study of the theory of transport phenomena in gases. In particular, we have continued the study of quantum effects, density effects, and the effects of internal degrees of freedom on the values of the transport coefficients.

In previous studies, we have developed expansions of the transport cross-sections in powers of the square of Planck's constant. Explicit expressions for the classical term and the first two quantum corrections have been obtained. The evluation of these coefficients for a realistic potential function is now being carried out on the CDC 1604. The program is essentially complete and is now being debugged. The resulting tables will be useful in the rapid evaluation of quantum effects on the transport coefficients in the intermediate temperature range where the effect is small but significant.

At sufficiently low temperatures the first term in the series referred to above differs from the usual classical expression. This is due to an effect of three classical turning points on the cross-section, which remains even in the limit $h \longrightarrow 0$. This surprising result is discussed in detail in the report TCI-69G. This manuscript has been submitted for publication in the Journal of Chemical Physics.

In collaboration with R. B. Bernstein and S. Imam-Rahajoe, the quantum mechanical expressions for the transport cross-sections have also been evaluated at lower temperatures using the Lennard-Jones potential. This evaluation was carried out by direct evaluation of the phase shifts and summation of the series. The result is a set of tables of the omega integrals as functions of the reduced temperature, T^*, and the dimensionless quantum parameter, Λ^*. These tables are described in the report TCI-59, which is the manuscript of a paper submitted for publication in the Journal of Chemical Physics.

We have also continued our study of the density effects on the transport coefficients. Expressions and numerical values of the viscosity and thermal conductivity second virial coefficients were obtained by Hoffman in his Ph.D. thesis, TCI-48. Two papers based on this thesis have been submitted for publication in the Physics of Fluids and a third is in preparation. The numerical results obtained by Hoffman agree reasonably well with the experimental values at the high temperatures. At low temperatures considerable disagreement occurs. This disagreement is very probably due to the effect of bound states which have not been considered properly in the theoretical development. We are continuing our study at this point and have some ideas which are not yet well developed.

We are also continuing our study of the effects of internal degrees of freedom on the transport coefficients. We have obtained an explicit expression for the quantum mechanical differential cross-section for collisions between loaded spheres. This will be used to obtain expressions for the transport properties of such a gas, which will be compared with the known classical expressions. We are also continuing our study of the inelastic collisions between a proton and a hydrogen atom, as a prototype of a more complex collision process.

SAUL T. EPSTEIN

CURRENT AND CONTEMPLATED MINOR RESEARCH PROJECTS

1) Application of the first order shielding approximation to the calculation of various dipole matrix elements in Helium. This project is underway in collaboration with K. Sando.

2) Application of the first order shielding approximation to the calculation of various one-electron properties of excited states of the Helium and Lithium isoelectronic series.

3) Preliminary to an investigation of various questions in the theory of magnetism. (See (7) below) we are calculating the magnetic susceptibility of H_2^+ in collaboration with Bowen Liu.

4) A detailed investigation of the one-body density matrix for three electrons and six natural spin orbitals is being conducted in collaboration with Mr. J. D. Garcia.

CURRENT AND CONTEMPLATED MAJOR RESEARCH PROJECTS

5) We propose to investigate the structure of light atoms using what one may call the "pair approximation". In principle the procedure is essentially that being pursued by O. Sinanoğlu but differs greatly in the details of the approach. We plan to use a variational wave function of the Hylleraas type involving inter-electronic coordinates r_{ij} explicitly. However, in any one term of the wave function we would allow a given index i to be paired with only another particular index j, i.e. we allow only pair

correlations in the wave functions. It is hoped that this physically reasonable approximation will facilitate integrations. This problem is being pursued with Mr. J. Karl and Dr. J. Rasiel.

6) There are many problems in quantum chemistry where it would seem that perturbation theory should apply and yet it is not quite clear how to proceed. For example, consider the long range forces between atoms. Here the natural way of partitioning the Hamiltonian into an unperturbed part H_o and a perturbation yields an H_o which is not symmetric in the electrons - surely an undesirable feature. A similar problem occurs in the discussion of the scattering of an electron by an atom. In each of their situations, however, one is in possession of a presumably good zero order wave function which is physically satisfactory (has the correct symmetry). We propose to investigate whether or not one can find in a practical way an optimal H_0 (optimal say in giving the best convergence of perturbation theory) of which Ψ_o is an eigenfunction. More precisely, there is no difficulty, at least formally, in finding any number of H_o's of which Ψ_o is the eigenfunction. The problem is in deciding which to use. A solution of this problem would also have application to the program of using Hartree-Fock wave functions as the first step in a perturbation procedure.

7) As a by-product of a recent investigation into the gauge properties of variational calculations we have formulated a criteria for the choice of an optimal gauge when one is dealing with limited basis sets. It would appear of interest to try this in practice.

JOHN GRAVES*

Theories of the conformation of proteins have been discussed by Scheraga, Schellman (The Proteins, 2nd Ed. H. Neurath Ed.) and others. These theories have been used to discuss the model systems of polyamino acids. In these homopolymers the change of conformation from a helix to a random coil is more amenable to quantitative measurements and to theoretical analysis than are the changes in proteins.

The equilibrium between any two states of a system is related to the free energy change by the well known relation $\Delta F^o = \Delta H^o - T \Delta S^o = RT \ln K_{eq}$. In these theories attempts are made to estimate the contributions to ΔH^o and to ΔS^o from different parts of the structure in the different conformations. A division of group type that has been made for the helix-random coil transition of polypeptides is: a) peptide backbone with associated hydrogen bonds; b) polar side group interactions; c) hydrophobic side group interactions; d) electrostatic interactions of charged groups. Covalent linkages between cystine side chains, of course, also play an essential role in determining conformation.

The helix-coil transition of polyamino acids is often termed "melting" and the melting temperature is defined as that having equal amounts of the helix and coil, K = 1 and $\Delta F = 0$. Then $T_m = \frac{\Delta H_T}{\Delta S_T}$ ΔH_T and ΔS_T may each be considered to have

- - - - -

* Dr. John Graves' research is supported by an N.I.H. grant.

a fixed contribution per monomer unit in the chain plus an end correction. There are four less hydrogen bonds than amino acid residues in the chain and the $\Delta H_{total} = (n - 4) \Delta H_{residue}$ has been used. The entropy has been considered to have less correction, namely $\Delta S_{total} = (n - 1) \Delta S$ residue, because there is one less peptide link, about which folding may change, than amino acids in the chain. The different end correction predicts an increase of melting temperature with increasing chain length, which is observed.

An experimental examination of this question would be to measure the melting temperature, the sharpness of melting, and the heat of melting (by sensitive calorimetry) of homopolymers of different chain length and of different amino acids. A further estimate of the heat of melting is given from the sharpness of melting, (α = fraction of total polymer in helix form) $\left(\frac{\partial \alpha}{\partial T}\right)_{T=T_{tr}} = \frac{\Delta H}{4RT^2}$. This discussion assumes the approximation that ΔH_{total} and ΔH_{res} are independent of temperature, which is [probably] not true.

Comparing different homopolymers might give some indication of the contributions of hydrogen bonding in the backbone and interactions of side-chains within the same helix. Because such helices have a known geometry they would also be a suitable early object of analysis by theory of the various contributions to intermolecular forces in polymers. Depending upon the comparison with experimental results at this stage, consideration could be undertaken of more complex heteropolymers.

JOHN HARRIMAN*

General areas of research interests include the calculation of approximate molecular wave functions, especially in systems with an odd number of electrons and the theory of magnetic effects in molecular systems: relativistic equations and their reduction to approximate form, and the best ways of describing possible effects. Higher order and time dependent effects in ESR spectroscopy are of both theoretical and experimental interest.

Current Theoretical research activities are:

1) Developing a computer program to calculate the spin density matrix for the eigenstate of total spin obtained by projecting an unrestricted Hartree-Fock single determinantal wave function. The theoretical basis for this is now available so present work is directed toward finding an efficient method of calculation.

2) An expression is also available for the spinless component of the second order density matrix for a projected, unrestricted Hartree-Fock function. The diagonal expansion is known and is quite simple if the natural orbitals of the first order spinless component (charge density matrix) are used as a basis. Several possibilities using these results are being investigated in the hope that the natural orbitals and the other independent parameters characterizing the projected state wave function can be calculated directly. If this can be done the method will provide a way of doing extended Hartree-Fock calculations. A matrix approach similar

* Professor Harriman's experimental research receives support from sources other than NASA.

to McWeeny's steepest descent method appears most promising.

3) A review and reformulation of the theory of energy absorption in paramagnetic resonance is being prepared. It is hoped that this will provide a basis for a more general and more rigorous theory of relaxation in systems where exchange, internal rotations, etc., occur at a rate which is neither very fast nor very slow on the time scale of the problem.

Another theoretical investigation will be carried out in connection with anticipated experimental work. The present generally available theories of magnetic (relativistic) effects in poly-electronic systems are not valid beyond second order in the fine structure constant. Formally correct but unjustified perturbation treatment going beyond this order have been used to describe certain anomalous observed behavior. This procedure will be checked theoretically and by careful experimental measurements.

JOSEPH O. HIRSCHFELDER

1) Estimation of Intermolecular Forces Between Complex Molecules

(In collaboration with Drs. William A. Sanders, John L. Graves, Debbie F. Tuan, Delano P. Chong, and Mr. Michael Twerdochlib)

A great deal is known empirically about the forces between simple spherical, or almost spherical, molecules such as the noble gases, H_2, O_2, N_2, NO, CH_4, etc. This information is obtained by using statistical mechanics to interpret: the second virial coefficient and the viscosity of gases; the crystal structure of the crystals as determined by x-ray and electron diffraction; and the Debye frequencies of the crystal lattice. However, very little is known about the forces between larger or more complex molecules. Crude quantum mechanical calculations indicate that the forces between conjugate double bond molecules are very peculiar indeed. At large separations their energy of interaction passes through a series of maxima and minima as the molecules move parallel to one another or as they are rotated with respect to each other. At intermediate separations conjugate double bond molecules exchange electrons. For three or more conjugate double bond molecules the interactions are characterized by the exchange of excitons and polarons. However, one does not need to go to pi-bond molecules in order to display our state of ignorance. Indeed, we know surprisingly little about the interactions of simple hydrocarbon molecules: ethane, propane, butane, etc.

We are embarking upon a big program to use statistical mechanics to interpret the existing experimental data in terms of a rather simple assumed functional form for the energy of interaction containing a small number of adjustable parameters. This form for the intermolecular energy will be based upon simple quantum mechanical notions. For example, as a starting point we might decompose the energy of interaction into the sum of: (a) direct electrostatic; (b) polarization or induced; (c) dispersion or fluctuation; (d) resonance; (e) charge exchange; (f) valence or chemical; (g) magnetic and relativistic. Of these the valence forces are the most difficult to estimate. At least in the beginning we shall assume the "perfect pairing" approximation which often goes by the name of the valence bond method or the vector model and is treated formally in Chapter 13 of Eyring, Walter and Kimball, Quantum Chemistry, (John Wiley, 1944). Whereas the valence method has not been successful in explaining the structure of normal molecules, it seems eminently suited to the treatment of intermolecular forces. Mason and Vanderslice have used this approach quite successfully in estimating the energy of interaction of O and N atoms with O_2, N_2, and NO molecules and the resultant properties of air at extremely high temperatures; also, they have estimated the energy of interaction of H atoms with H_2 molecules and the resultant properties of hydrogen at extremely high temperatures. For each interacting electron pair one assumes an exchange integral having the form $A \exp(-aR)$ where A and a are constants to be adjusted empirically. The perfect pairing approximation leads us to suppose that the valence energy of interaction is a sum of the atom-atom terms between each of the atoms in the two interacting molecules. It seems likely at the present time that such an approach will be successful in explaining the energies of interactions between valence saturated molecules. This, for example, would include all of the aliphatic hydrocarbons. However, it seems likely that the perfect pairing approximation will have to be refined in order to consider non-localized pi-electron interactions realistically. In any case, the exchange integrals involving pi-electrons should be angle dependent.

The van der Waals forces are easy to estimate in terms of bond-bond interactions where one takes into account the parallel and perpendicular bond polarizabilities so that the energy of interaction between two bonds depend upon their relative angles.

Thus, we shall gradually build up a scheme for predicting the energy of interaction between arbitrary molecular structures. The exchange integrals which we determine empirically from the properties of one substance will be useful in the prediction of the properties of a great many other molecules. We feel that this program will build up in importance. At first both our experimental fits and our theoretical treatment will be crude, but gradually we will build up in sophistication. Eventually, we hope that the full treatment can be carried out by purely mechanical calculations.

2) <u>Magnetic and Relativistic Intermolecular Forces</u>.

(In collaboration with William J. Meath).

Most of the things we know about intermolecular forces apply only to molecules in their ground states. Collisions between molecules in excited states (which occur frequently in the upper atmosphere and at high temperatures) involve magnetic and relativistic spin-spin, spin-orbital, and orbit-orbit as well as retardation effects. Meath and I are currently making a systematic study of the different types of intermolecular forces through terms of order α^2 (where α is the fine structure constant, 1/137) which are given by first order perturbation theory using the Breit-Pauli Hamiltonian. Many new types of forces appear. For example, Meath and I find an energy of interaction which varies as the inverse fourth power of the separation and occurs in all molecular collisions including interactions of ground state noble gases. Then there is an energy of interaction which Stephen and Mavroyannis first discovered, which is specific for optically active molecules. We will investigate each of these terms and the conditions under which they are important.

During the next year we intend to consider the interaction energy terms of higher order in α which involve the use of quantum electro-dynamics. Specifically, we are wondering about the possible importance of Lamb-shift effects on intermolecular forces, as well as Feynman diagram terms involving the creation and annihilation of two-photons. Such terms cannot be obtained from the Breit-Pauli Hamiltonian.

Once we have obtained the two-photon energy terms, we can examine the errors which are currently being made in nuclear magnetic resonance and in electron-spin resonance by using the

Breit-Pauli Hamiltonian together with second order perturbation theory and ignoring some of the two-photon Feynman transitions.

We feel that this work is essential in order to have a thorough understanding of the nature of intermolecular forces. Undoubtedly, some of our results will be important in the understanding of upper atmosphere and planetary atmospheric spectroscopy.

3) Different Screening Constants for Different Physical Properties. (In collaboration with William A. Sanders).

One of the most important problems in quantum mechanics is the calculation of accurate expectation values of properties other than energy. It remains an open question whether it is necessary to use Hartree-Fock wave functions for such calculations. We have explored the possibility of using simpler wave functions with embedded screening constants, where different screening constants are used for the calculation of different properties. The properties of the family of two-electron atoms (and ions) provide a convenient test of the numerical accuracy of different methods of calculation. As a basis of comparison William A. Sanders and I used the calculations of C. W. Scherr and R. E. Knight (University of Texas), which are based on a perturbation expansion in powers of the reciprocal of the nuclear charge. They have determined a large number of properties accurate through the sixth order.

A. Dalgarno (Queen's University, Belfast) has suggested that a screening constant be chosen so as to make the first order perturbation correction vanish for the property under consideration.

Peter D. Robinson (who is presently at the University of Sussex, but did some of this work at the University of Wisconsin Theoretical Chemistry Institute) has shown that this choice is equivalent to the requirement that the zeroth order wave function satisfy a hypervirial relation, where the hypervirial generator is related to the property through a differential equation. The Dalgarno procedure gives excellent numerical results when applied to the calculation of properties represented by positive definite operators.

For those one-electron properties associated with positive definite operators, the Dalgarno procedure gave expectation values which were too small. This suggested maximizing the expectation value calculated with the zeroth order plus first order wave functions. In some cases slight improvements were obtained in this way, but the amount of additional work required casts some doubt on the practicality of the method.

The idea of using different screening constants for different properties dates back to the early days of quantum mechanics. In 1927 Pauling proposed a systematic procedure for determining the screening constants. His method was applicable to any property which, for a hydrogen-like atom, would vary as some power of Z and as some other power of the principal quantum number. He predicted rather accurately the molar refraction, diamagnetic susceptibility, atomic scattering factors, etc., for atoms and ions throughout the whole periodic table. Unfortunately, Pauling's method of adjusting the screening constants does not seem to be currently applicable. However, the principle still remains valid that the screening is small near the nucleus and becomes large at large separations.

The amazing thing about these screening constants which are varied so as to minimize the energies of an atom is that the screening constant for a particular principal azimuthal quantum number remains constant from atom to atom. See, for example, J. C. Slater, (Quantum Theory of Atomic Structure, McGraw-Hill, 1960, Volume 1, page 348 et seq). In calculating the expectation values of properties other than energy, we expect to find the same constancy of the screening constants as we go from atom to atom. In WIS-TCI-71, November 1964 (submitted for publication to the J. Chem. Phys.) Sanders and I calculated the set of screening constants for two-electron atoms and ions. We are now continuing to work on a determination of the additional screening constant required for the ground state of three-electron atoms and ions. We hope to continue this for a sequence of many-electron atoms. We believe that the screening constants so obtained will be useful in calculating a variety of atomic problems. But what is more important from our standpoint is the possibility of using the simple atomic wave functions with screening constants as a starting point for calculating the structure and properties of molecules (by means of perturbational-variational techniques).

4) The Use of Non-local Potentials in Perturbation Theory.

Saul T. Epstein has interested me in the following problem, which I find very intriguing. In most practical quantum mechanical problems we are given an approximate wave function, and we are asked to estimate the energy and true wave function of the system as accurately as possible. In principle this can be done with the use of the Rayleigh-Schrödinger perturbation method. As a first step, we must find the unperturbed Hamiltonian. For example, we might use the Sternheimer procedure setting

$$h_0 = \epsilon_0 + T - (T \psi_0 / \psi_0)$$

where ϵ_0 is a constant, T is the kinetic energy operator, and ψ_0 is the approximate wave function. If we require that the potential energy be local, h_0 is the only possible unperturbed Hamiltonian. However, if non-local potentials are permitted, there are an infinite number of Hamiltonians for which ψ_0 is an eigenfunction. For example, the possible sets of Hamiltonians H_0 would be equally permissible where

$$H_0 = h_0 + \sum_j a_j |\psi_j \rangle\langle \psi_j |$$

Here the ψ_j are the other eigenfunctions of h_0 and the constants a_j are arbitrary. Different choices of a_j lead to different values for the second and higher order energies and lead to different functions for the perturbed wave functions. K. Kumar (<u>Perturbation Theory and the Nuclear Many Body Problem</u>, North-Holland Publishing Company, 1962) shows how one choice of the a_j makes the Rayleigh-Schrödinger procedure equivalent to the Brillouin-Wigner; another choice makes it equivalent to the Feenberg; indeed, it is possible to choose the a_j so as to make the first order perturbed wave function equal to the exact wave function for the perturbed system.

The terms $|\Psi_j\rangle\langle\Psi_j|$ in H_0 are examples of non-local potentials. Thus it is clear that the very nature of a perturbation problem can be drastically altered by the presence of non-local potentials. In the Hartree-Fock self-consistent field treatment non-local potentials occur in a natural and physically meaningful way. We are exploring the general significance of non-local potentials in perturbation calculations with the hope that we can simplify the calculations and increase the rate convergence.

DANIEL D. KONOWALOW

1) Journal Publications:

(a) "Correlation Energy of Two-Electron Systems" (with J.L.J. Rosenfeld) published in the 1 December 1964 issue of J. Chem. Phys.

(b) "An Improved Intermolecular Potential Function" (with Sergio Carra') published in Nuovo Cimento 34, 205 (1964).

Abstract - An intermolecular potential function of the form

$$\Psi(r) = \epsilon \frac{n+b}{b} \left(\frac{r_m}{r}\right)^n \left[\frac{n}{n+b} e^{b(1-r/r_m)} - 1\right]$$

is presented. With N = 6 this form is simpler and more realistic than the extensively used Buckingham (exp-6) potential. The classical second virial coefficient has been calculated $b = 6.0(0.5)9.0$ and $0.4 \leq kT/\epsilon \leq 400$. The potential parameters are determined for some rare gases for experimental second virial coefficients and the separation between nearest neighbors in the crystal lattice at 0^{o}K.

2) T.C.I. Technical Reports:

(a) WIS-TCI-56G was submitted for publication in J. Chem. Phys.

Abstract - From an examination of some simple, correlated, variational wave functions for He we find: (1) it is unimportant to satisfy the correlation cusp condition to obtain a low energy; (2) a wide variety of correlation functions are very nearly the same in the range $0 \leq r_{12} \leq 3$ a.u., thus implying a simple structure for the Coulomb hole.

(b) WIS-TCI-74 - "Intermolecular Potential Functions for Nonpolar Molecules, II" (with Sergio Carra') to be submitted to the Physics of Fluids. Abstract - "Most likely" Morse potential functions for Ne, Ar, Kr, Xe, N_2, and CH_4 are determined from experimental second virial coefficient $[B(T)]$ and viscosity $[\eta(T)]$ data. By employing variants of the usual statistical fitting procedures, the elucidation of different features of the potentials is emphasized. Our "most likely" potentials give a better description of the experimental $B(T)$ and $\eta(T)$ and repulsive scattering potentials than do those based largely on crystal properties. The Morse potential is apparently less suitable than the Kihara potential for reproducing the experimental $B(T)$ and $\eta(T)$ at least for Ar; neither model is able to reproduce both properties within the limits of experimental error. A comparison is made with other selected model potentials.

3) Current Activities:

(a) The method developed earlier by Konowalow and Carra' (WIS-TCI-74) is applied to the determination from experimental second virial coefficient and viscosity data of "spherically averaged" intermolecular potential functions (based on the Morse model) for a number of hydrocarbons. Relationships between the critical constants V_c and T_c and the Morse potential parameters are discussed. For the homologous series of n-alkanes the characteristic length parameter σ may be approximated by $\sigma(n) \approx 3.5 + 0.5\ (n-1)\ \mathrm{\AA}$, $1 \leq n \leq 8$ where n is the number of carbon atoms in the chain.

(b) With Hirschfelder and Tu, I have reconsidered the "b' equation of state"

$$(P + a/V^2)\ (V - b + b'/V) = RT$$

for gases promulgated recently by Hirschfelder et. al.* It has proved quite successful in reproducing experimental isotherms for a wide variety of substances. One may set $b'/b^2 = 0.362$ thus reducing the number of adjustable constants by one. Preliminary calculations show that this two-parameter modification of the van der Waals equation of state is able to reproduce isotherms for a wide range of densities very nearly as well as the "b' equation".

(c) There has been widespread interest in the analysis of wavefunctions into their natural orbitals. It is of some interest to analyze the LCAO-MO-SCF-CI wavefunction for H_2 ground state due to Ransil and Fraga and to connect it to the natural expansion of Hirschfelder and Löwdin which is valid for very large separations. The result will be a "most likely" wavefunction for H_2 in natural orbital form.

4) Long-range research program:

My long-range program has two main aspects:

(a) The first is the elucidation of inter- and intra-molecular (atomic) potentials. The semi-empirical approach (for example, some of the work quoted earlier) will be continued, but at a perceptibly decreased rate. The main effort will be directed toward

- - - - -

* Ind. Eng. Chem. 50, 375 (1958).

interactions of astrophysical interest. My studies of the electron-electron correlation problem are directed toward finding a practical method of calculating some important intermolecular interactions *a priori* and thus to provide a firm basis for more-realistic semi-empirical calculations than is presently possible.

(b) The second main interest is in reducing to practice the quantum mechanical calculation of chemical and physical properties of atoms and molecules.

STUART E. LOVELL

During the period July 1, 1964 through December 31, 1964, work continued on the theoretical study of high energy atom-ion collisions. This work has been done in collaboration with M. B. McElroy of the Kitt Peak National Observatory, Tuscon, Arizona.

In particular, the following three reactions were investigated:

$$H^+ + H(1s) \longrightarrow H(1s) + H^+ \qquad (1)$$

$$H^+ + H(1s) \longrightarrow H(2s) + H^+ \qquad (2)$$

$$H^+ + H(1s) \longrightarrow H^+ + H(2s). \qquad (3)$$

The first is an example of resonance charge transfer, the second, non-resonance charge transfer, and the third, excitation. The method used was to expand the wave function for the colliding system in a truncated two center expansion on atomic eigenfunctions. To date, we have included only the 1s and 2s functions on both centers. This grossly simplified picture of the actual collision is used so as to allow us to focus our attention on the importance of coupling between the various states. Cross sections have been calculated for the three reactions given above at energies between 1 and 400 KEV. Two state cross sections, i.e. where the expansion includes only the initial and final states, had been previously calculated by other investigators. We have calculated cross sections including the various possible combinations of three states and also all the four states. For the nonresonance processes, the three and four state cross sections are substantially higher at low energies than the two state results. This seems to agree better with the limited experimental data which is available.

The calculation of these cross sections is a major computational effort. Each cross section for one energy requires about 30 minutes of CDC 1604 time. We are, at the moment, modifying our program so as to make it easier to include more states in the expansion and also so that the program can be used for systems other than proton-hydrogen.

A report on the results of our three state calculations has been made [1] and also is in press (Proc. Royal Soc.). A report on the four state results is being prepared. We might note here that in the four state results we see certain very interesting symmetry effects. Our original purpose in investigating the proton-hydrogen system was that it forms a simple model for more complicated (many electron) systems. These symmetry effects will persist in the more complicated systems and this shows that our model is serving its original purpose.

This work can be expanded in many directions. Most immediately we plan to include the 2p states in our expansion (still for proton-hydrogen system). Beyond that we can easily study deactivation,

- - - - -

1. Report: "The Importance of Coupling for Inelastic Collisions between Protons and Hydrogen Atoms", S. E. Lovell, M. B. McElroy. Kitt Peak National Observatory, Tuscon, Arizona, (1964).

Note: The above report and the Journal article resulting from it both give explicit recognition of the support of this work by NASA and TCI. A copy of this report has been given to Mr. Harry Harrison of NASA.

i.e., the reverse of the excitation reaction, alpha particle - hydrogen atom collisions, and proton-hydrogen minus ion collisions, this last being our current choice for the first two electron system to study. Many other systems can be suggested but we feel that the above are the most feasible and interesting at this time.

SUMMARY OF EXPENDITURES AND UNLIQUIDATED COMMITMENTS

July 1, 1964 - December 31, 1964

NASA Grant NsG-275-62

	Expenditures	Unliquidated Commitments	Totals
Salaries	$ 92,404.95	$ 17,246.85	$ 109,651.80
Computing Services	5,761.69	8,604.09	14,365.78
Travel	1,763.19	176.55	1,939.74
Publications	443.75	1,838.13	2,281.88
Services	465.03	8.09	473.12
Supplies	1,128.09	417.18	1,545.27
Communications	249.55	303.96	553.51
Honoraria for Consulting Services	4,079.05	390.00	4,469.05
Total Direct Costs	$ 106,295.30	$ 28,984.85	$ 135,280.15
Overhead*	21,259.06	5,796.97	27,056.03
Total Costs	$ 127,554.36	$ 34,781.82	$ 162,336.18

* 20% of Total Direct Costs

APPENDIX A - Theoretical Chemistry Institute Short-Term Visitors

During the period 1 July 1964 through 31 December 1964

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Prof. Bruno Linder Dept. of Chemistry Florida State University Tallahassee, Florida	6/15/64 - 8/1/64	Interaction Between Polar Molecules.
Dr. Jan Stecki Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland	7/1/64 - 7/31/64	General Equations of Irreversible Evolution of Classical Gases and the Bogolyubov-Prigogine-Resibois Markovian Regime.
Dr. David M. Schrader Dept. of Chemistry State University of Iowa Iowa City, Iowa	7/1/64 - 8/31/64	
Prof. Alberte Pullman Directrice de Recherche Centre National de la Recherche Scientific, Paris	7/6/64 - 8/14/64	Lecture series: Electronic Aspects of Biochemistry - General Theory.
Prof. Bernard Pullman, Director Institute de Biologie Physico-Chimique Laboratoire de Chimie Quantique Universite de Paris, Paris	7/6/64 - 8/14/64	Lecture series: Electronic Aspects of Biochemistry - Biological Applications.
Prof. George Hall Dept. of Mathematics University of Nottingham Nottingham, England	7/8/64 - 8/14/64	Spin - Other Orbit Coupling in Molecules. Introduction to a New Theory of Unimolecular Decomposition.
Howard S. Taylor Dept. of Chemistry University of Southern Calif. University Park Los Angeles 7, Calif.	7/15/64 - 7/17/64	
Prof. Robert G. Parr Dept. of Chemistry The Johns Hopkins University Silver Spring, Maryland	7/30/64	The Physical Origin of the Barrier to Internal Rotation in the Ethane Molecule.
Profs. Akiko and Kimio Ohno Faculty of Science University of Hokkaido Sapporo, Japan	8/3/64 - 8/7/64	

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Dr. Paul E. Cade Dept. of Physics University of Chicago Chicago, Illinois	8/10/64	The Electronic Structures of Diatomic Molecules
Dr. Peter D. Robinson Dept. of Mathematics University of Sussex Falmer, Brighton, Sussex England	9/7/64 - 10/6/64	
Prof. H. F. Hameka John Harrison Laboratory of Chemistry University of Pennsylvania Philadelphia, Pennsylvania	9/21/64 - 9/22/64	The Role of Molecular Vibrations of Optical Rotation.
Prof. Arthur A. Frost Dept. of Chemistry Northwestern University Evanston, Illinois	11/19/64	Series Solution for Non-Separable Schrödinger Equations.
Prof. I. Amdur Dept. of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts	11/24/64	Scattering of High Velocity Helium and Argon Molecular Beams.
Peter R. Fontana Dept. of Physics University of Michigan Ann Arbor, Michigan	7/12/64 - 7/24/64 8/2/64 - 8/8/64 11/30/64 - 12/4/64	Configuration Interactions in Lithium. Irreducible Tensors and Their Use in Atomic Calculations.
Prof. Robert Yaris Washington University St. Louis, Missouri	12/1/64	The Linked Cluster Expansion, Unitartity and the Electron Correlation Problem.
Dr. Paul S. Bagus Argonne National Laboratory Argonne, Illinois	12/7 - 8/64	SCF Excited States.

APPENDIX B - University of Wisconsin Theoretical Chemistry Institute

Staff - July 1, 1964 - December 31, 1964

NAMES	TITLES
Research Staff:	
Joseph O. Hirschfelder	Professor of Chemistry; Director, Theoretical Chemistry Institute
Charles F. Curtiss	Professor of Chemistry; Associate Director, Theoretical Chemistry Institute
Richard B. Bernstein	Professor of Chemistry
Saul T. Epstein	Professor of Physics
William Byers Brown	Associate Professor of Chemistry
Frank C. Andrews	Assistant Professor of Chemistry
John E. Harriman	Assistant Professor of Chemistry
Stuart E. Lovell	Assistant Professor Computer Sciences
Daniel D. Konowalow	Assistant Director, Theoretical Chemistry Institute

Post-Doctorate Staff:

Margaret L. Benston University of Washington Ph.D. 1964	Project Associate
Delano P. Chong Harvard University Ph.D. 1963	Project Associate
John L. Graves University of Chicago Ph.D. 1956	Project Associate
David K. Hoffman University of Wisconsin Ph.D. 1964	Project Associate
Karl H. Kramer Universität Bonn Bonn, West Germany Ph.D. 1962	Research Associate
William A. Lester The Catholic University of America Ph.D. 1964	Project Associate
Peter M. Livingston University of Wisconsin Ph.D. 1961	Project Associate
Yecheskel Rasiel Case Institute of Technology Ph.D. 1964	Project Associate
William A. Sanders Purdue University Ph.D. 1961	N.S.F. Post-Doctoral Fellow
Debbie F. Tuan Yale University Ph.D. 1961	Project Associate
Günter G. Weber University of Tübingen Tübingen, Germany Ph.D. 1961	Project Associate

Computing Staff:

Mrs. Carol E. Constable	Project Assistant
Mrs. Wanda W. Giese	Project Assistant
Mrs. Nahida H. Gordon	Project Assistant
Mrs. Florence N. Greville	Project Assistant
Mrs. Linda E. Hulbert	Project Assistant
Mrs. Merline D. McCloud	Project Assistant
Mrs. Carol B. Monash	Project Assistant (Ending Oct. 1964).

Graduate Students:

David E. Bennett	Research Assistant
Raymond Beshinske	Research Assistant
Tai Yup Chang	Research Assistant
Roger W. Fenstermaker	Teaching Assistant
Lloyd M. Holm	Teaching Assistant
John H. Huntington	Research Assistant/Teaching Assistant
R. Soesanto Imam-Rahajoe	Agency for International Development Scholarship
John H. Karl	Research Assistant
Sungwoon Kim	Research Assistant
Donald J. Kouri	Research Assistant
Bowen Liu	Research Assistant
William D. Lyon	Research Assistant
Robert Matcha	Research Assistant
William J. Meath	Research Assistant
Mac Brown Milleur	Teaching Assistant
John Mueller	Research Assistant

Graduate Students:

George Nazaroff	Research Assistant
Thomas O'Brien	Research Assistant
Russell Pack	N.S.F. Fellow
Robert E. Roberts	Teaching Assistant
Kenneth Sando	Research Assistant/Teaching Assistant
Michael Twerdochlib	Research Assistant
Theodore G. Waech	Research Assistant
Thomas C. Wallace	Teaching Assistant/N.S.F. Fellow
Pearl S. C. Wang	Research Assistant
Ronald J. White	N.A.S.A. Fellow
Herbert T. Wood	N.S.F. Fellow

Office Staff:

Mrs. Karen A. Rick	Project Assistant
Mrs. Gloria M. Lawton	Stenographer II
Miss Linda L. Becker	Stenographer II
Mrs. Mary A. Wilson	Typist III
Mrs. Colleen E. Kotnour	Clerical Assistant

APPENDIX C - Summary of Research at the Theoretical Chemistry Institute During the Period July 1, 1964 through December 31, 1964

COMMENT ON CORRELATION FUNCTIONS FOR THE HELIUM ATOM by Daniel D. Konowalow and Jean L. J. Rosenfeld (supported by Air Force and NASA).

Report No. WIS-TCI-56G dated 7 July 1964

Submitted for publication to J. Chem. Phys.

PERTURBATION THEORY OF ONE-ELECTRON DIATOMIC MOLECULES. I. HOMONUCLEAR by Robert L. Matcha, William D. Lyon, and Joseph O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-57 dated 14 July 1964

ABSTRACT

The application of perturbation theory to separable systems is discussed. First order wave functions of H_2^+ are calculated using various zeroth order approximations. The energy through third order is calculated and compared with energies determined by Bates, Ledsham and Stewart. Agreement is exact for the best zeroth order approximation.

CALCULATION OF SPIN-SPIN INTERACTION INTEGRALS by David M. Schrader (supported by NASA).

Report No. WIS-TCI-58 dated 16 July 1964

Published in J. Chem. Phys., 41, 3266 (1964).

NUMERICAL EVALUATION OF QUANTUM EFFECTS ON TRANSPORT CROSS SECTIONS by S. Imam-Rahajoe, C. F. Curtiss, and R. B. Bernstein (supported by A.E.C. and NASA).

Report No. WIS-TCI-59 dated 1 August 1964

Scheduled to be published in the 1/15/64 issue of J. Chem. Phys.

ABSTRACT

Quantum mechanical calculations of the transport cross sections $Q^{(1)*}$ and $Q^{(2)*}$ and the associated $\Omega^{(n,t)*}$ integrals are presented for a Lennard-Jones (12,6) potential. The computations are made for three values of the quantum parameter Λ^* (=1,2,3), and include the effects

of statistics. The quantum effects become quite important at reduced temperatures T^* below about unity. The quantum corrections to the integrals are negative at moderate temperatures, but become positive at higher temperatures.

VARIOUS METHODS OF SOLVING A FIRST ORDER PERTURBATION EQUATION by Boris Musulin (supported by NASA).

Report No. WIS-TCI-61G dated 18 August 1964

PERTURBED OPERATORS IN HILBERT SPACE by Theodore W. Palmer (supported by NASA).

Report No. WIS-TCI-62 dated 25 September 1964

ABSTRACT

This report reviews the theory of perturbed operators in an abstract Hilbert space and some important applications of the theory to quantum chemistry. It is intended to serve as an introduction to the original papers of Rellich, Sz-Nagy, Kato and others. The theory developed by these authors, which is apparently little known among quantum chemists, rigorously justifies the use of Rayleigh-Schrödinger perturbation theory in many important quantum chemistry problems.

FOCUSING OF SYMMETRIC TOP MOLECULES WITH THE ELECTRIC SIX-POLE FIELD by K. H. Kramer and R. B. Bernstein (supported by U.S.A.E.C., NASA and Bureau of Naval Weapons, A.P.L.)

Report No. WIS-TCI-63G dated 1 September 1964

Scheduled to be published in the 1/15/65 issue of J. Chem. Phys.

ABSTRACT

The electric six-pole field is applied to the focusing of beams of symmetric top molecules via the first order Stark effect. Molecules capable of a specified degree of orientation can be selected according

to the voltage applied to the electrodes of the six-pole field. The molecules CH_3I and CHI_3 have been chosen to illustrate the focusing action for prolate and oblate symmetric tops.

AN INTEGRAL EQUATION APPROACH TO THE PLASMA SELF CONSISTENT FIELD PROBLEM by Peter M. Livingston (supported by NASA).

Report No. WIS-TCI-64 dated 3 September 1964
Submitted for publication to Phys. of Fluids.

ABSTRACT

The self consistent field problem of a "collisionless", fully ionized, single component plasma is treated by means of a Green's function technique. The latter describes the streaming motion of non-interacting electrons in a time dependent, homogeneous, applied electric field. A formal perturbation series solution to the Liouville equation, obtained by iteration, is then considered in the limit of large number and volume. For a problem time scale of the order of the inverse plasma frequency, only the terms in the perturbation series describing the collective interaction survive the limiting process, and therefore a time-reversible, hierarchy of integral equations is recovered for the various orders of distribution functions. The non-linear integral Vlassov equation follows from the first member of this hierarchy and a factorization assumption on the initial distribution function.

An approximate solution to the Vlassov equation is developed in terms of the solutions to the linearized form of this equation. In these calculations, the Green's function has been simplified by averaging it over a period of the external field.

Finally, after defining the inverse dielectric function by the relationship between the "dressed" and "free" electron number densities, a correction term of order e^2 to the usual linear theory result is found. It is expected that this correction will be found useful in subsequent studies of non-linear electrical behavior in plasmas.

INTERNAL ENERGY OF REACTION PRODUCTS BY VELOCITY ANALYSIS. I. SCATTERED KBr^* FROM THE CROSSED MOLECULAR BEAM REACTION K + HBr by Arthur E. Grosser, Anthony R. Blythe and Richard B. Bernstein (supported by U.S.A.E.C. and NASA).

Report No. WIS-TCI-65G dated 9 September 1964

Scheduled to be published in the 2/15/65 issue of J. Chem. Phys.

ABSTRACT

The velocity distribution of excited KBr^* formed in reactive collision between crossed beams of velocity-selected K and thermal HBr has been measured as a function of scattering angle for two different initial relative kinetic energies, E. The most probable value of the recoil velocity of the KBr^* yields the final relative kinetic energy E' and thus the value of the most probable "collision-exothermicity" $Q \equiv E' - E = \Delta D_o^o - \Delta E_{int}$, where ΔE_{int} is the most probable value of the internal energy change. Results of a series of experiments at E = 1.9 kcal/mole gave Q = 0.5 $\pm$ 0.5 kcal/mole (out of an _a priori_ range from -1.9 to +5.1 kcal/mole) and thus the most probable internal (excitation) energy for the KBr : $E^*_{KBr} = 4.6 \pm 0.7$ kcal/mole. The observed angular velocity distributions of KBr imply that the differential reactive scattering cross section in the center-of-mass (c.m.) system is predominantly confined to low angles (i.e., "forward

hemisphere", with the KBr^* product preferring the direction of the incident K in the c.m.). Less extensive experiments at E = 3.2 kcal/mole served to confirm these conclusions.

INTERMOLECULAR FORCES by Joseph O. Hirschfelder (supported by N.I.H.)

Report No. WIS-TCI-66 dated 23 September 1964
Scheduled to be published in the Proceedings of the International Summer Institute of Molecular Biophysics, Squaw Valley, Calif., Aug. 17-18, 1964, Academic Press.

ABSTRACT

It is difficult to provide a quantitative explanation of the forces between biologically active molecules because these molecules are large, complex, and immersed in an aqueous solution. There are seven types of intermolecular forces which must be considered: (1) direct electrostatic, (2) polarization or induced, (3) dispersion or fluctuation, (4) resonance, (5) valence or chemical, and (6) magnetic and relativistic. Each is considered in detail. In addition, the effects of solvation are discussed.

CALCULATED ELASTIC SCATTERING CROSS SECTIONS FOR THE Li^+-He SYSTEM by G. G. Weber and R. B. Bernstein (supported by NASA and U.S.A.E.C.)

Report No. WIS-TCI-67 dated 6 October 1964
Accepted for publication in J. Chem. Phys.

ABSTRACT

Calculations of the energy dependence of the total (and differential) elastic scattering cross sections for the Li^+-He system have been carried out for a number of assumed interaction potentials (from the literature). All of these are known to yield good fits to existing mobility data, sensitive primarily to the long-range r^{-4} term in

the potential. The present results show that the total quantum cross sections (as well as the angular distributions) are quite sensitive to the potential also at short range (e.g. $r < 4\text{Å}$), even at low collision energies (E<1eV). In particular, the behavior of the extrema in the total cross sections offers a means of discrimination among the potentials.

ROTATIONS, REPRESENTATIONS, AND WIGNER COEFFICIENTS by C. F. Curtiss
Report No. WIS-TCI-68G dated 28 September 1964

THE EFFECT OF THREE TURNING POINTS ON SEMI-CLASSICAL SCATTERING by C. F. Curtiss (supported by NASA).
Report No. WIS-TCI-69G dated 26 October 1964
Accepted for publication by J. Chem. Phys.

ABSTRACT

When three turning points occur in the effective potential, the region between the two inner turning points is associated with classically bound trajectories or quantum mechanically metastable states. The effect of this portion of the effective potential energy curve on the phase shifts and transport cross sections is discussed.

ON THE SOLUTION OF THE BBGKY EQUATIONS FOR A DENSE CLASSICAL GAS by Frank C. Andrews (supported by NSF).
Report No. WIS-TCI-70 dated 30 October 1964
Submitted for publication to J. Chem. Phys.

ABSTRACT

The low order BBGKY equations are solved formally by being expressed in the form of integral equations. A density expansion is introduced to break the hierarchy. The functional equation for f_2 and two equivalent evolution equations for f_1 are formulated

directly, correct to second order in the density. The results are compared with other treatments of the first density corrections to the Boltzmann equation and to the f_2 equation. The physical implications of the derivations are discussed in detail.

DIFFERENT SCREENING CONSTANTS FOR DIFFERENT PHYSICAL PROPERTIES, I by William A. Sanders and Joseph O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-71 dated 13 November 1964
Submitted for publication to J. Chem. Phys.

ABSTRACT

Expectation values of properties other than energy are calculated for the ground state of the two-electron atom with arbitrary nuclear charge. The calculations are designed to test the use of simple wave functions with embedded screening constants, where different screening constants are used for different properties. The results are compared with the perturbation expansion of Scherr and Knight, who have determined a large number of properties correct through sixth order.

Dalgarno has suggested that a screening constant be chosen so as to make the first order perturbation correction vanish for the property under consideration. Robinson has shown that this choice is equivalent to the requirement that the zeroth order wave function satisfy a hypervirial relation, where the hypervirial generator is related to the property through a differential equation. This procedure gives excellent numerical results for properties having positive definite operators.

For one-electron properties with positive definite operators, Dalgarno's method gives expectation values which are too small. When applicable, slight improvements are obtained by maximizing the expectation value calculated with the zeroth plus first order wave functions.

SOME REMARKS ON THE USE OF THE VARIATIONAL PRINCIPLE FOR THE SECOND ORDER ENERGY by Jean H. Epstein and Saul T. Epstein (supported by NASA).

Report No. WIS-TCI-72 dated 16 November 1964

ABSTRACT

It is pointed out that if one uses an approximate ground state wave function in the familiar variational principle for the second-order energy, that the approximate energy need have no special relationship to the exact energy (it may be larger or smaller). Further it is shown that in some cases even with full use of the variation principle, good accuracy of the ground state wave function does not imply corresponding accuracy of the approximate energy.

AN APPRAISAL OF THE FOPIM FAST-CONVERGING PERTURBATION METHOD by Peter D. Robinson, John H. Huntington and Joseph O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-73 dated 19 November 1964

Accepted for publication in J. Chem. Phys.

ABSTRACT

The practicality of the First-Order-Perturbation-Iteration-Method (FOPIM) is appraised. After the first iteration, the expectation value of the energy is given by a non-analytic function of the perturbation parameter λ. The asymptotic expansion of this function gives the enrgy accurately up to O(λ^8).

The convergence of the asymptotic expansions is discussed. Two examples are considered: a perturbed ground state hydrogen atom, and a perturbed ground state linear harmonic oscillator.

MORSE POTENTIAL FUNCTIONS FOR NONPOLAR GASES by Daniel D. Konowalow and Sergio Carra' (supported by NASA and U.S.A.F.)

Report No. WIS-TCI-74 dated 7 December 1964
Submitted for publication to Phys. of Fluids.

ABSTRACT

"Most likely" Morse potential functions for Ne, Ar, Kr, Xe, N_2, and CH_4 are determined from experimental second virial coefficient $[B(T)]$ and viscosity $[\eta(T)]$ data. By employing variants of the usual statistical fitting procedures, the elucidation of different features of the potentials is emphasized. Our "most likely" potentials give a better description of the experimental B(T) and $\eta(T)$ and repulsive scattering potentials than do those based largely on crystal properties. The Morse potential is apparently less suitable than the Kihara potential for reproducing the experimental B(T) and $\eta(T)$ at least for Ar; neither model is able to reproduce both properties within the limits of experimental error. A comparison is made with other selected model potentials.

Additional Publications During the Period July 1, 1964 - December 31, 1964

"Variational Wave Functions Satisfying Hypervirial Theorems in Fixed Source Meson Theory" by D. MacArthur and Saul T. Epstein, Proc. of Midwest Conf. Theor. Phys., 1964.

"Thermodynamic Properties of Mixtures of Hard Spheres" by J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys., 41, 133 (1964).

"Upper and Lower Bounds for Rayleigh-Schrödinger Perturbation Energies" by K. M. Sando and J. O. Hirschfelder (WIS-TCI-39), Proc. Natl. Acad. of Sci., 52, 434 (1964).

"Some Remarks on Quantum Mechanics and the Principle of Equivalence" by Saul T. Epstein, Phys. Letters, 11, 233 (1964).

"Hartree-Fock Hamiltonians and Separable Nonlocal Potentials" by Saul T. Epstein, J. Chem. Phys., 41, 1045 (1964).

"General Solutions of the Hamilton-Jacobi Equation" by Saul T. Epstein, Am. J. Phys., 32, 688 (1964).

"Quantum Corrections to the Transport Cross Sections" by H. T. Wood and C. F. Curtiss (WIS-TCI-34A), J. Chem. Phys., 41, 1167 (1964).

"Variational Solutions to the Brillouin-Wigner Perturbation Differential Equations" by W. J. Meath and J. O. Hirschfelder (WIS-TCI-35AG), J. Chem. Phys., 41, 1628 (1964).

"Observation of Rotational De-Excitation of D_2 Using Crossed Molecular Beams" by A. R. Blythe, A. E. Grosser, and R. B. Bernstein (WIS-TCI-54G), J. Chem. Phys., 41, 1917 (1964).

"Gibbs Third Variational Principle in Statistical Thermodynamics" by W. Byers Brown (WIS-TCI-53), J. Chem. Phys., 41, 2945 (1964).

"Correlation Energy of Two-Electron Systems" by D. D. Konowalow and J. L. J. Rosenfeld (WIS-TCI-50), J. Chem. Phys., 41, 3556 (1964).

"Kinetic Theory of Dense Gases III. The Generalized Enskog Equation" by D. K. Hoffman and C. F. Curtiss, Phys. of Fluids, Dec. 1964 issue.

"Index of Refraction of Helium in the Shielding Approximation" by Boris Musulin and Saul T. Epstein (WIS-TCI-55), Phys. Rev., 136, A966 (1964).

"X-Ray Scattering by a Crystal in an Electric Field" by A. D. Buckingham (WIS-TCI-26), Acta Crystallographica, 17, 960 (1964).

APPENDIX D

The attached letters from the Dean of the Graduate School, the Chairman of the Department of Chemistry, and the Chairman of the Department of Chemical Engineering indicate the close ties which we have with many of the University Departments and the cooperation which we are receiving from the University of Wisconsin administration.

THE UNIVERSITY OF WISCONSIN
MADISON 53706

DEPARTMENT OF CHEMISTRY

November 30, 1964

Mr. John R. Craig
Research Program Manager
Office of Grants and Research Contracts
National Aeronautics and Space Administration
Washington, D. C.

Dear Mr. Craig:

I would like at this time on behalf of the Department of Chemistry of the University of Wisconsin to express our gratitude to NASA for making it possible for the Theoretical Chemistry Institute to continue its outstanding activities. Though the Institute functions as a separate unit, it is closely integrated with the Department. The contributions of those Institute staff members who are professors of chemistry and teach courses and direct the research of graduate students are obvious. But in addition there are many indirect benefits to our Department through informal consultations of the theoretical staff with other professors and other students. Moreover, the presence of this powerful nucleus of theoretical talent strengthens us enormously and helps us to bring in and retain on our staff outstanding investigators in all branches of chemistry. The experimentalists in our Department can in turn interact favorably with the Institute to everyone's mutual advantage.

Sincerely yours,

John D. Ferry
John D. Ferry
Chairman, Department of Chemistry

JDF/bjg

The Graduate School THE UNIVERSITY OF WISCONSIN · MADISON, WISCONSIN 53706 TEL: 262-2433

November 27, 1964

Mr. John Craig
Manager Research Program
National Aeronautics and Space Administration
Code SC
Washington, D. C. 20546

Dear Jack:

I want to take this opportunity to tell NASA how much their support of Professor Hirschfelder's Theoretical Chemistry Institute has been appreciated by the University. This Institute has greatly strengthened the Chemistry Department in the theoretical area by increasing the amount of research, providing consulting for the rest of the Department and bringing in distinguished visitors.

Professor Hirschfelder's group has also interacted strongly with other groups on the campus (Physics, Mathematics and Engineering, for example) and has increased local interest in space research.

Cordially,

Robert A. Alberty

Robert A. Alberty
Dean

RAA:ds

The University of Wisconsin

EGE OF ENGINEERING
ARTMENT OF CHEMICAL ENGINEERING
DISON 53706 262-1092

November 30, 1964

Mr. John R. Craig
Research Program Manager
Office of Grants and Research Contracts
National Aeronautics and Space Administration
Washington, D. C.

Dear Mr. Craig:

Professor Hirschfelder has asked me to write you a letter regarding the interaction between the Chemical Engineering Department and the Theoretical Chemistry Institute.

This is easy to do, since there has been a strong tradition of cooperation and exchange between our two groups, and our department has made frequent use of the facilities of the T.C.I. and their staff.

On several occasions Professor Hirschfelder has made his computing staff available to me and my students. I often use the library and reprint file of the TCI and scarcely a week goes by that I do not have some occasion to consult with some member of the staff regarding a technical question. Professors Lightfoot and Stewart, and their students, have from time to time called upon TCI staff members for help in connection with multicomponent diffusion problems. Other areas where our interests overlap include equation of state, conbustion phenomena, statistical mechanics, transport properties, and fluid mechanics.

The T.C.I. has played an invaluable role on the campus here at the University of Wisconsin.

Sincerely,

R Byron Bird

R. Byron Bird, Chairman
Chemical Engineering Department

RBB:jol